1920
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S. S. Gandheker

Derivatives of Dihydronaphthalene

DERIVATIVES OF DIHYDRONAPHTHALENE

BY

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1920

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G15

UNIVERSITY OF ILLINOIS

Jan. 31 1920

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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ENTITLED Derivatives of dihydronaphthalene

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

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Acknowledgment

The writer wishes to express his indebtedness to Professor Roger Adams for his guidance in this work and for his genial attitude which made association with him always pleasant.

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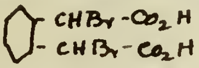
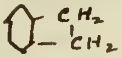
Part 1

Introductory

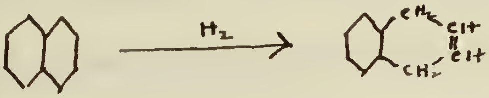
Primarily research is intended to give the student abili to handle original problems. Though each problem is an individual one and lacks competition to a certain extent the problem itself oftentimes is a sufficient incentive to spend on it most of the extra time the student has at his disposal. It has achieved its main aim if it makes the student self-reliant and independent in his thinking.

The original idea in synthesising these compounds was to prepare O-phenylene di-acetic acid and then through the di-bromide  to close the ring  which would have been a very interesting reaction. This method of preparing the di-acetic acid however was a failure as will be seen later. In preparing most of these compouds the writer sometimes altered the proportions or changed the methods to get better results and it has been so far with success.

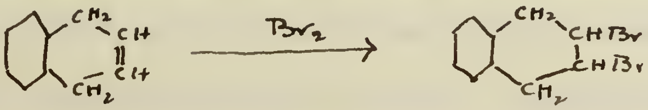
Historical and theoretical

In 1895 Bamberger and Lodter worked on the alycyclic derivatives of naphthalene in the laboratory of the University of Munich and they seem to have synthesised a great many compounds All this has been published in the "Annalen der chemie" Vol 288.

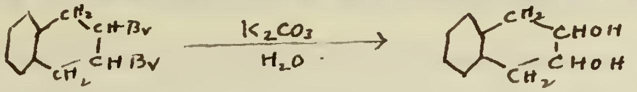
Naphthalene is reduced with sodium and absolute alcohol to the dihydronaphthalene



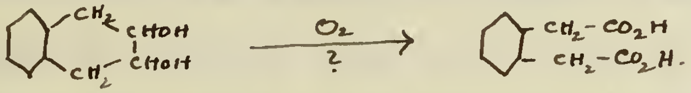
When this reduction product is brominated it gives the dibromide



The dibromide is then terated with potassium carbonate and water and the dihydronaphthalene glycol is prepared.

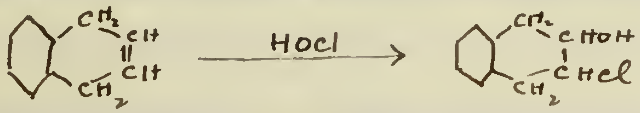


Bamberger and Lodter by oxydising this glycol with dichromate and sulphuric acid got the O-phenylene diacetic acid.



This reaction does not go. The oxydising agents were changed and dilute solutions were used so as not to use a too strong an agent In all these reactions the whole compounds evidently must have gone to pieces.

From the dihydronaphthaleme the chlorohydrin is prepared



Practical

Preparation of dihydronaphthalene

The first attempt was made by placing 22.5 grams of sodium cut into fine pieces in a round bottomed 2-literflask and connecting it with 2 condensers is "series" thus avoiding the use of a large condenser. The top of the condenser is protcted from moisture by means of a $CaCl_2$ tube. 15 grams of naphthalene is dissolved in 300 c.c. of absolute alcohol and this is heated to boiling. This hot solution is then poured in small amounts from the top of the condenser .The alcohol boils vigorosly and the addition of more solution is delayed till the boiling has subsided There was no heatimg necessary and the heat generated is sufficient to keep the flsk hot and also to melt all the sodium. Later on experience showed that the use of a separatory funnel running

through the stopper beside the condenser and long enough to reach the bottom of the flask was advantageous. In this way the tedious process of pouring through the condenser was avoided and even here the addition of the hot solution had to be controlled from time to time to prevent the gas bubling throughthe funnel. The sodium was used in lumps as it melts owing to the heat of the reaction. After a little experience the writer used 150 grams of naphthalene 225 grams of sodium and about 2½ liters of absolute alcohol. This operation of reducing takes from 3-4 hours.

After it is completely reduced and after all the sodium is decomposed it is steam-distilled when the alcohol containing a little of the reduction product comes over first. The second fraction consists mostly of dihydronaphthalene and some unchanged naphthalene. The first fraction is heated on a steam bath to a small volume and added to the second. This is then extracted with ether and the extrct consists of all the reduction product and a little naphthalene. On evaporating off the ether the dihydronaphthalene is pure enough for most purposes. If however a pure product is desired this can be distilled and the product distlles at 212°C It melts at 15.5° C. The writer found this method of seperating the product better than freezing the ether extract and getting it out that way. The last time naphthalene was reduced the writer was able to get 132 grams of dihydronaphthalene from 150 grams of naphthalene.

Preparation of dihydronaphthalene dibromide

This addition product was originally prepared by dissolving 25 grams of dihydronaphthalene in chloroform and treating drop by drop a solution of 28 grams of bromine in chloroform. A better

method however is to keep the dihydronaphthalene dissoved in a large amount of chloroform in an Erlenmeyer flask and keep in anothe a little over 30 grams of bromine. This bromine is then aspirated through the dihydronaphthalene by suction very slowly. As the bromine vapor comes into the solution it is decolorised quickly and towards the end very very slowly. At this stage the suction is stopped and the chloroform is subjected to spontaneous evaporation near a hood. The solution is then left in the ice-box or in a cool place to crystallise. The dibromide crystallises very slowly in a week's time in small needles. Part of the solution which is a dark brown oil fails to solidify and is probably some other derivative. The dibromide melts at 73°-74° C. 48 grams of the dihydronaphthalene gave 17 grams of the dibromide.

Preparation of dihydronaphthalene glycol

30 grams of dihydronaphthalene dibromide is placed in about 1½ liters of boiling water in a 3 liter flask. About 20-25 grams of potassium carbonate are ~~is~~ dissolved in 100c.c. of water and added to the flask mixing it well. The flask is then refluxed over an oil bath for 10 hours by which time the dibromide would have disappeared. The flask is then disconnected and subjected to steam distillation. In this way some reduced naphthalene and other derivatives are removed and the glycol remains behind. The residue is then evaporated to a small volume and the glycol crystallised This is of a light brown color and recrystallises from hot water as pure white tablets. It melts at 135° c The yield is very good in the case.

Oxydation of the glycol

This oxydation was tried by dissolving 10 grams of the glycol in a little acetic acid and water and then treating with 44 grams of potassium dichromate and 300 grams of 20% sulphuric acid in three stages. Only 20 grams of the dichromate and 135 grams of the acid are added at first. After 2 days standing during which time the color of the solution becomes a little greenish 12 grams of the dichromate and 100 grams of the acid are added. After about two days standing again the rest of the dichromate and acid are added. After a few days standing the solution is filtered and agi agitated with large amounts of ether. Evaporation of the ether extract however gave no substance. The above reaction was tried 6 or 7 times without any success. Then the oxydising agents were chaged. A quantitative proportion of the glycol and pottassium permanganate were used. The permanganate was added slowly to the glycol solution with constant shaking, This too did not give any results. Then a milder agent was tried PbO_2 and dilute HCl. This too failed. In all these reactions the oxydation must have gone too far rupturing the ring altogether.

It is very striking that during the first oxydation a compound seperated from the solution which crystallises to very fine needles from alcohol. It is insoluble in water soluble in hot alcohol and ether and melts at 70° C. It is neither an acid nor a ketone . Its composition as determined (C,34.5% H,3.5%) does not throw any light on its nature. In succeeding oxydations the writer could not make this compound though it looks very strange.

Preparation of dihydronaphthalene chlorohydrin

This reaction consists in the addition of HOCl to the

dihydronaphthalene. The HOCl being very un-stable the preparation of this compound presents many difficulties. 400 grams of bleaching powder is agitated with 2 liters of water at 40° C. and after a day's standing in the dark is treated with 300 grams of potassium carbonate. After a time this is filtered by suction and is treated with 320 grams of boric acid and well agitated. The crystalline borate is filtered off and to the the clear solution 25 grams of dihydronaphthalene is added.

The HOCl may also be prepared by passing chlorine into a weighed amount of NaOH in a flask surrounded by a freezing mixture till the exact quantitative amount of chlorine is added. This is best done by counterbalancing the weighed amount of NaOH in a flask and the freezing mixture in one pan of a balance and then putting additional weights equivalent to the weight of chlorine to be added in the other pan and then passing chlorine till the pans are in balance. This is done to avoid any excess of chlorine which may interfere with the reaction. This is then treated with a little over the quantitative amount of boric acid, filtered and to the filtrate the dihydronaphthalene is added.

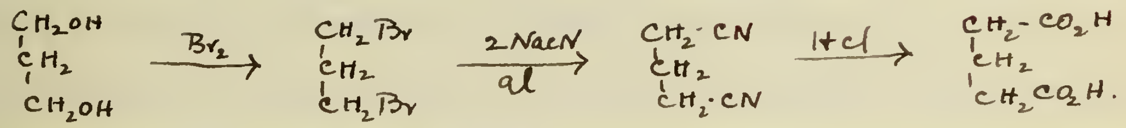
The chlorohydrin seperates in the bottom and is filtered off. It crystallises from water in fine white needles which melt at 111° C. The yield is very poor and may be improved if the HOCl can be made without decomposition.

Part 2

Preparation of Glutaric acid

Theoretical

This acid was prepared from trymethylene glycol through the bromide and the cyanide



Another method of preparing the acid by condensing malonic ester with formaldehyde in the presence of diethyl amine did not work. A heavy viscous product is obtained in place of the crystalline acid . The first method yields much better results.

Practical

Preparation of trimethylene bromide

One mole of the trimethylene glycol is treated with three moles of 48% hydrobromic acid and to this is slowly added one mole of sulphuric acid. After a time this is distilled. First HBr comes over. The second fraction consists of the dibromide. The dibromide layer is separated, washed a few times with water, dried overnight with $CaCl_2$ and fractionated collecting the fraction boiling between 163°-165° C. The yield is 68%

Preparation of the cyanide and the acid

One mole of the bromide is treated with two moles of powdered NaCN and about three times the volume of alcohol and refluxed for 6-8 hours on an oil bath. Then it is distilled . The alcohol and some of the unchanged bromide comes over first and the last fraction is entirely trimethylene cyanide.

Later on the following procedure was adopted. The first two fractions are distlled from the cyanide preparation up to 140°-150° C. Now the residue consists entirely of the cyanide and

NaBr and a little NaCN. To this residue 2½ volumes of HCl are added and connected to a condenser. After a little while the whole thing turns to a solid mass and no heating is necessary. After some time the HCl is evaporated on the water bath and the residue is dissolved in absolute alcohol to extract the glutaric acid. Then a known amount of $Ba(OH)_2$ is added to prevent esterification and the alcohol distilled. The barium salt is dissolved in water , decolorised with animal charcoal,decomposed by the quantitative amount of sulphuric acid and the glutaric acid crystallised from hot water. It is recrystallised again. It crystallises in very small white tablets which melt at 93°-94° C. The yield is 11% in terms of the bromide and is higher when we calculate in terms of the cyanide.

Summary

Part 1

Reduction of naphthalene to dihydronaphthalene with Na and absolute alcohol

Formation of the dihydronaphthalene dibromide by the addition of bromine to dihydronaphthalene

Preparation of dihydronaphthalene glycol by the action of K_2CO_3 and water

Attempts at oxydation of the glycol to O-phenylene diacetic acid by $K_2Cr_2O_7$ and H_2SO_4, $KMnO_4$ and H_2O, PbO_2 and HCl

Preparation of dihydronaphthalene chlorahydrin

Part 2

Preparation of trimethylene bromide and cyanide from trymehtylene glycol

Saponification of trimethylene cyanide to glutaric acid

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